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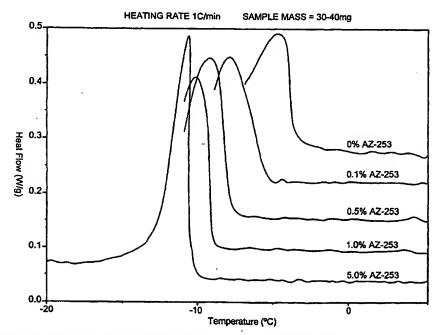
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[Continued on next page]

(54) Title: COMPOSITION



(57) Abstract: There is provided a composition comprising a fatty acid and a flow improver.

# WO 01/38461 A1



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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

#### COMPOSITION

The present invention relates to the improvement of the low temperature operability of fatty acids in a composition.

In many industrial applications additives are incorporated in compositions of interest. The additives are generally incorporated to provide a functional effect to the composition. For example, an additive may modify the physical properties of the composition, for example the additive may modify the viscosity, or melting/boiling point, of the composition.

An additive for a fuel composition is disclosed in GB 2121807. The additives are obtained by reacting an amine compound, with a copolymer comprising recurrent units (A) from an alkyl ester of an unsaturated monocarboxylic acid and/or a vinyl ester of a saturated monocarboxylic acid, recurrent units (B) from diisobutylene and recurrent units (C) from an unsaturated alpha, beta-dicarboxylic compound. The additives are used for lowering the cloud point of middle distillates having a molecular weight from 1,000 to 50,000. It is taught by GB 2121087 that the additives may inhibit the formation of paraffin crystals in the middle distillates. It is disclosed that the paraffin crystals form at a lower temperature than they otherwise would in the absence of the additive.

It has now been recognised that fatty acids themselves provide operational difficulties when incorporated in a composition. For example, in certain circumstances, fatty acids may exhibit operability difficulties at low temperatures. At temperatures of up to 10°C components of fatty acids can precipitate from a fuel composition and settle on the bottom of a vessel containing the composition. The heterogeneity resulting from such precipitation and settlement creates difficulties in handling and accurate material usage. Furthermore, should it be required to transfer the fatty acid composition from one place to another difficulties may be experienced as filters may block. The blockage may result in consequent catastrophic pump seizure. These disadvantages are particularly experienced and problematic when fatty acids are stored in a large tank which may be exposed to low temperatures. In this particularly problematic environment, solvent dilution or heating the tanks to overcome this problem are cost prohibitive and may be ineffective or impractical.

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Fatty acids are used in fuels as non-metallic, phosphorus-free additives to enable refiners to maintain or improve lubricity quality. However, the problems of fatty acid precipitation and settlement is not limited to the field of fuels, fatty acids are utilised in, for example, adhesives, alkyd resins, detergents, cleaners, inks, coatings, lubricants, metalworking fluids, mining, oil exploration, paper production, polyamide resins, road building, rubber processing, corrosion inhibitors and surfactants.

The present invention addresses the problems of the prior art.

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In one aspect the present invention provides use of a flow improver for the prevention and/or inhibition of the crystallisation of a fatty acid.

In a further aspect the present invention provides a composition comprising a fatty acid or an ester, amine salt or amide derivative thereof and a flow improver.

By the term "flow improver" it is meant a material which will lower the operability temperature of a composition comprising a fatty acid and the flow improver when compared to the composition in the absence of the flow improver, evidenced, for example by lowering the pour point, the cloud point, the wax appearance temperature, the cold filter plugging point (hereinafter CFPP), differential scanning calorimetry (DSC) or the Low Temperature Flow Test (LTFT) temperature of a fuel, or will reduce the extent of wax settlement in a fuel, especially a middle distillate fuel.

By the term "lower the operability temperature" it is meant the temperature at which fatty acid precipitates from a given composition is lowered or the amount of fatty acid which precipitates from a given composition at a given temperature is reduced.

By the term "prevention and/or inhibition of crystallisation of a fatty acid" it is meant that the flow improver, specifically a cloud point depressant, lowers the temperature at which the fatty acid begins to crystallise or for a given temperature lowers the amount of fatty acid which crystallises. The additives continue to work as the temperature of the material cycles with changes in ambient temperature.

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#### FLOW IMPROVER

Flow improvers suitable for use in the present invention are described in each of WO-A-94/17159, WO-A-95/03377, WO-A-93/14178, WO-A-94/10267, WO-A-99/28416, WO-A-95/33805, WO-A-96/18708, WO-A-96/18706, WO-A-96/18708, EP-A-0356256, EP-A-0673990, EP-A-0261957, US-A-3048479, GB-A-1263152, GB-A-1112808, and GB-A-2121808.

Preferably the flow improver is present in the composition in an amount of less than 10 wt%, preferably 0.0l to 5.00 wt.%, preferably 0.05 to 3.00 wt.%, preferably 0.10 to 2.00 wt%, based on the total weight of the composition.

In a preferred aspect the present invention the flow improver is selected from wax modifiers, including cloud point depressants and wax anti-settling additives; cold flow improvers including distillate fuel cold flow improvers, pour point depressants, wax appearance temperature depressants, cold filter plugging point (CFPP) depressants, low temperature flow test (LTFT) temperature depressants and mixtures thereof. In a more preferred aspect, the flow improver is diesel fuel cloud point depressant.

Numerous classes of flow improvers, especially middle distillate flow improvers, are suitable for use in the present invention.

Preferably the flow improver of the present invention is selected from (A) ethyleneunsaturated ester copolymers, (B) comb polymers, (C) polar nitrogen compounds, (D) hydrocarbon polymers and mixtures thereof.

The preferred flow improvers are discussed in WO 95/33805 and will now be described in further detail.

30 (A) Ethylene-unsaturated Ester Copolymers,

The ethylene-unsaturated ester copolymers are preferably ethylene-unsaturated ester copolymers having, in addition to units derived from ethylene, units of the formula  $-CR_1R_2-CHR_3$ -

35 wherein R<sub>1</sub> represents hydrogen or methyl, R<sub>2</sub> represents COOR<sub>4</sub>, wherein R<sub>4</sub>

4

represents an alkyl group having from 1 to 9 carbon atoms, which is straight chain or, if it contains 3 or more carbon atoms, branched, or  $R_2$  represents OOCR<sub>5</sub>, wherein  $R_5$  represents  $R_4$  or  $R_5$  or  $R_5$  represents  $R_4$  or  $R_5$  represents  $R_6$  or  $R_7$  represents  $R_8$  or  $R_8$  represents  $R_8$  or  $R_8$  represents  $R_8$  or  $R_9$  represents  $R_9$  r

These may comprise a copolymer of ethylene with an ethylenically unsaturated ester, or derivatives thereof. An example is a copolymer of ethylene with an ester of a saturated alcohol and an unsaturated carboxylic acid, but preferably the ester is one of an unsaturated alcohol with a saturated carboxylic acid. An ethylene-vinyl ester copolymer is preferred; an ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl hexanoate, or ethylene-vinyl octanoate copolymer is preferred. Preferably, the copolymer contains from 5 to 40 wt.% of the vinyl ester, more preferably from 10 to 35 wt.% vinyl ester. A mixture of two copolymers may be used. The number average molecular weight of the copolymer, as measured by vapour phase osmometry, may be 1,000 to 10,000, preferably 1,000 to 5,000. If desired, the copolymer may contain units derived from additional comonomers, e.g. a terpolymer, tetrapolymer or a higher polymer, for example where the additional comonomer is isobutylene or disobutylene.

The copolymers may be made by direct polymerisation of comonomers, or by transesterification, or by hydrolysis and re-esterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene-vinyl hexanoate and ethylene-vinyl octanoate copolymers may be made in this way, e.g., from an ethylene-vinyl acetate copolymer.

#### (B) Comb Polymers

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By the term "comb polymers" it is meant a polymer in which branches containing hydrocarbyl groups are pendant from a polymer backbone, and are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Plate and V P Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

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Generally, comb polymers have one or more long chain hydrocarbyl branches, e.g., oxyhydrocarbyl branches, normally having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt.

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Preferably, the comb polymer is a homopolymer having, or a copolymer at least 25 and preferably at least 40, more preferably at least 50, molar percent of the units of which have, side chains containing at least 6, and preferably at least 10 carbon atoms.

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The comb polymer may contain units derived from other monomers if desired or required.

Preferably the comb polymer is or comprises a copolymer of (i) maleic anhydride, fumaric acid, itaconic acid or a mixture thereof and (ii) another ethylenically unsaturated monomer, e.g., an α-olefin, including styrene, or an unsaturated ester, for example, vinyl acetate or homopolymer of fumaric or itaconic acids. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerised with e.g., maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

The acid or anhydride group of the comb polymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol or 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures.

The comb polymers may be furnarate or itaconate polymers and copolymers such for example as those described in EP-A-0153176, EP-A-0153177 and EP-A-0225688, and WO-A-91/16407.

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Further fumarate comb polymers include copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, including polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of  $C_{14}/C_{16}$  alkyl groups, made, for example, by solution copolymerising an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer

WO 01/38461

6

PCT/GB00/04328

with the alcohol or mixture of alcohols, which are preferably straight chain alcohols. When the mixture is used it may be a 1:1 by weight mixture of normal  $C_{14}$  and  $C_{16}$  alcohols. Furthermore, mixtures of the  $C_{14}$  ester with the mixed  $C_{14}/C_{16}$  ester may be used. In such mixtures, the ratio of  $C_{14}$  to  $C_{14}/C_{16}$  may be in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight. The particularly preferred comb polymers are those having a number average molecular weight, as measured by vapour phase osmometry, of 1,000 to 100,000, more especially 1, 000 to 30,000.

Other suitable comb polymers are the polymers and copolymers of α-olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above. Other examples of comb polymers are hydrocarbon polymers, e.g., copolymers of ethylene and at least one α-olefin, the α-olefin preferably having at most 20 carbon atoms, examples being n-decene-1 and n- dodecene- 1. Preferably, the number average molecular weight of such a copolymer is at least 30,000 measured by Gel Permeation Chromatography (GPC). The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

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# (C) Polar Nitrogen Compounds

Preferably the polar nitrogen compound is or comprises an oil-soluble polar nitrogen compound carrying one or more, preferably two or more, substituents.

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Preferably the substituents are of the formula  $>NR_{13}$ , where  $R_{13}$  represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom.  $R_{13}$  preferably represents an aliphatic hydrocarbyl group containing 12 to 24 carbon atoms. The oil soluble polar nitrogen compound is generally one capable of acting as a wax crystal growth inhibitor in fuels.

Preferably, the hydrocarbyl group is linear or slightly linear, i.e. it may have one short length (1-4 carbon atoms) hydrocarbyl branch. When the substituent is amino, it may carry more than one said hydrocarbyl group, which may be the same or different.

The term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups may be saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

The or each amino or imino substituent may be bonded to a moiety via an intermediate linking group such as -CO-, -CO<sub>2</sub>-, -SO<sub>3</sub>- or hydrocarbylene. Where the linking group is anionic, the substituent is part of a cationic group, as in an amine salt group.

When the polar nitrogen compound carries more than one amino or imino substituent, the linking groups for each substituent may be the same or different.

25 Suitable amino substituents are long chain C<sub>12</sub>-C<sub>40</sub>, preferably C<sub>12</sub>-C<sub>24</sub>, alkyl primary, secondary, tertiary or quaternary amino substituents.

Preferably, the amino substituent is a dialkylamino substituent, which, as indicated above, may be in the form of an amine salt thereof; tertiary and quaternary amines can form only amine salts. Said alkyl groups may be the same or different.

Examples of amino substituents include dodecylamino, tetradecylamino, cocoamino, and hydrogenated tallow amino. Examples of secondary amino substituents include dioctadecylamino and methylbehenylamino. Mixtures of amino substituents may be present such as those derived from naturally occurring amines. A preferred amino

8

substituent is the secondary hydrogenated tallow amino substituent, the alkyl groups of which are derived from hydrogenated tallow fat and are typically composed of approximately  $4\% C_{14}$ ,  $31\% C_{16}$  and  $59\% C_{18}$  n-alkyl groups by weight.

Suitable imino substituents are long chain  $C_{12}$ - $C_{40}$ , preferably  $C_{12}$ - $C_{24}$ , alkyl substituents.

Said moiety may be monomeric (cyclic or non-cyclic) or polymeric. When non-cyclic, it may be obtained from a cyclic precursor such as an anhydride or a spirobislactone.

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

# (D) Hydrocarbon Polymers

The hydrocarbon polymers may be made directly from monoethylenically unsaturated monomers or indirectly by hydrogenating polymers from polyunsaturated monomers, e.g., isoprene and butadiene.

Examples of hydrocarbon polymers are disclosed in WO 91/11488.

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Preferred copolymers are ethylene  $\alpha$ -olefin copolymers, having a number average molecular weight of at least 30,000. Preferably the  $\alpha$ -olefin has at most 28 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octene-1, isooctene-1, n- decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight, of other copolymerisable monomers, for example

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olefins other than α-olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer.

The number average molecular weight of the ethylene  $\alpha$ -olefin copolymer is, as 5 indicated above, preferably at least 30,000, as measured by get permeation chromatography (GPC) relative to polystyrene standards, preferably at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120, 000.

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The copolymer may have a molar ethylene content between 50 and 85 percent or the ethylene content may be within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

Preferred ethylene- $\alpha$ -olefin copolymers are ethylene- propylene copolymers with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000; especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

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The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. The polymers should be substantially amorphous.

Other suitable hydrocarbon polymers include a low molecular weight ethylene- $\alpha$ -olefin 25 copolymer, possibly with a number average molecular weight of at most 7500, preferably from 1,000 to 6, 000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate α-olefins are as given above, or styrene, with propylene again being preferred. The ethylene content may be from 60 to 77 molar percent, although for ethylene- propylene copolymers up to 86 molar percent by weight ethylene may be employed.

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In a further preferred aspect the hydrocarbon polymer is or comprises a terpolymer of (i) linear C16 or C18 alkene, (ii) a C18 methacrylate or acrylate, and (iii) a succinimide having a C18 carbon chain. In a more preferred aspect, the components (i), (ii) and (iii) are present in a ratio of approximately 1:1:1.

WO 01/38461

PCT/GB00/04328

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Previous performance has been demonstrated in their application to middle distillate fuels GB 2121807.

The hydrocarbon polymer may be a dialkyl dicarboxylic acid-vinyl acetate copolymers derived by polymerisation of vinyl acetate and mixed alcohol carboxylate 1 esters, with nalkyl groups of average number of carbon atoms ranging from 10 carbons to 30 carbons, preferably C4 to C8 dicarboxylic acids. These copolymers may include dialkyl fumarate-vinyl acetate copolymers derived by polymerisation of vinyl acetate and mixed alcohol fumarate esters, with n-alkyl groups of average number of carbon atoms ranging from 10 carbons to 30 carbons.

The hydrocarbon polymer may be a alkyl phenol resin or phenol aldehyde resin or phenol formaldehyde resin, preferably an oxalkylated amine with n-alkyl groups of average number of carbon atoms, ranging from 1 carbon to 30 carbons. For phenol formaldehyde resin, preferably the phenols are methylene linked. The n-alkyl groups have an average number of carbon atoms ranging from 20 carbons to 36 carbons, more specifically, ranging from 24 carbons to 28 carbons.

20 Preferably the hydrocarbon polymer is dissolved or is dispersed in an aromatic solvent.

The aromatic solvents in which the hydrocarbon polymer may be dissolved or dispersed may be Aromatic 150 available for example from Esso, Surasol or xylene.

It is within the scope of the invention to use a combination of two or more flow improvers selected from one or more of the different classes outlined above.

#### **FATTY ACID**

The fatty acid may be obtained from any suitable source. For example the fatty acid may be obtained or may be obtainable from an animal or a plant source. In a preferred aspect the fatty acid is obtained or is obtainable from rapeseed oil, coriander oil, soybean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef oil, tallow oil, fish oil, and mixtures thereof.

Preferably the fatty acid is selected from saturated, unsaturated, poly-unsaturated fatty acids, and mixtures thereof.

Preferably the fatty acid is selected from lauric acid, rosin acids myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid, erucic acid, eicosapentaenoic acid and mixtures thereof.

Preferably the fatty acid is selected from mixtures of fatty acids having a chain length of from 12 to 22 carbon atoms. More preferably the fatty acid is selected from mixtures of fatty acids having a chain length of from 16 to 18 carbon atoms.

In preferred aspect the fatty acid is selected from mixtures of fatty acids consisting of 10-80% oleic monounsaturated fatty acid, 10-80% linoleic di-unsaturated fatty acid, 0-80% saturated fatty acid and 0-80% rosin acid.

In a further preferred aspect the fatty acid is a tall oil fatty acid. Tall oil fatty acids typically comprise mixtures of fatty acids consisting of approximately 65% linoleic diunsaturated fatty acid, approximately 30% oleic mono-unsaturated fatty acid, approximately 2% saturated fatty acids and <2% rosin acid. Thus, in highly preferred aspect the fatty acid is selected from mixtures of fatty acids consisting of approximately 65% linoleic di-unsaturated fatty acid, approximately 30% oleic mono-unsaturated fatty acid, approximately 2% saturated fatty acids and <2% rosin acid.

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Preferably the saturated fatty acids are selected from stearic acid (C16) and palmitic (C18) acid.

Fatty acids are commercially widely available, for example from Unichema, Henkel,
Croda, and Oleofina. Tall oil fatty acids are typically available from Arizona Chemical,
Georgia Pacific, Hercules and Westvaco.

As the fatty acid solution cools, the flow improver of the present invention such as a cloud point additive, interacts with and alters the precipitating material's crystallisation onset temperature. This change retards crystal formation and growth, keeping the fatty

12

acids in solution, thereby preserving the operability of the solution. The fatty acids remain in solution available for pumping, injecting, or addition.

#### **COMPOSITION**

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In one aspect of the present invention the composition is substantially free of a bio-fuel. In this aspect the composition may be substantially free of fatty acid containing oils (triglycerides) or fatty acid esters which may act as a fuel.

The composition of the present invention may comprise one or more additional components applicable to the application of the composition. These additional components may be those known to one skilled in the art. The one or more additional components may be selected from detergents, one or more additional cold flow improvers, antioxidants, corrosion inhibitors, dehazers, demulsifiers, antifoaming agents, cetane improvers, conductivity improvers, metal deactivators, dyes, chemical markers, cosolvents, package compatibilisers, carrier oils, biocides, surfactants, buffers, lubricity additives including polycarboxylic acids, and mixtures thereof.

The composition may comprise one or more solvents, including organic solvents.

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As discussed above, the fatty acids may be used in many application areas. The composition of the present invention may be or may be utilised in an adhesive, alkyd resin, detergent, cleaner, fuel additive, ink, coating, lubricant, metalworking fluid, mining fluid, oil field exploration, paper treatment, polyamide resin, road building, rubber processing, corrosion inhibitor, surfactant or fuel.

#### **FUEL**

In a highly preferred aspect the present invention provides a fuel comprising a composition of the present invention. Preferably the fuel is selected from gasolines including motor, aviation, tractor, and marine fuels, and middle distillate fuels including diesel fuels, marine fuels, and heating oils. The fuel may a biofuel, such as a vegetable-based fuel oil, including a rapeseed methyl ester and vegetable oil; and mixtures thereof.

35 As described in WO 95/33805 a "middle distillate" refers to fuel oils obtainable in refining

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crude oil as the fraction from the lighter, kerosene or jet fuel, fraction to the heavy fuel oil fraction. The fuel oils may also comprise atmospheric or vacuum distillate, cracked gas oil or a blend, in any proportions, of straight run and thermally and/or catalytically cracked distillate. Examples include kerosene, jet fuel, diesel fuel, heating oil, visbroken gas oil, light cycle oil, vacuum gas oil, light fuel oil and fuel oil. Such middle distillate fuel oils usually boil over a temperature range, generally within the range of 100°C to 500°C, as measured according to ASTM D86, more especially between 150°C and 400°C.

In a further highly preferred aspect the present invention provides a fuel additive consisting of a composition of the present invention.

In a further highly preferred aspect the present invention provides a lubricity improver consisting of a composition of the present invention. At the recommended treat rates, the lubricity improver may demonstrate performance in Stanadyne and Bosch Pump Rig Lubricity tests, and High Frequency Reciprocating Rig, Ball on Cylinder Lubricity Evaluator, and Scuffing Load Ball on Cylinder Lubricity Evaluator bench tests. These products do not interact with engine lubricants, fuels, or other fuel additives, and are compatible with the constituent materials of the engine and fuel system.

In a further highly preferred aspect the present invention provides a lubricant composition consisting of a composition of the present invention.

In a further broad aspect of the present invention the fatty acid of the present invention may be partially or completely substituted by an ester, amine salt or amide derivative of a fatty acid.

The invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

30 Figure 1 is a graph;

Figure 2 is a graph;

Figure 3 is a graph;

Figure 4 is a graph;

Figure 5 is a graph;

# **EXAMPLES**

The following fatty acid compositions (FAC) were used in the Examples below

PROPERTY	FAC 1	FAC 2	FAC 3	
	PH	YSICAL PROPERTIES		
Acid Number	195	194	197	
Viscosity (cps 20°C)	27	27	20	
Saponification Number	198	197	199	
lodine Number (WIJS)	155	155	130	
	COMP	OSITIONAL PROPERTIES		
Rosin Acids %	0.8	1.8	0.9	
Unsaponifiables %	1.8	2.0	1.3	
Total Fatty Acids %	97	97	98	•
Polyunsaturated acids %	66	65	44	
Monounsaturated acids %	29	29	50	
Saturated %	2	2	2	
Other %		-	2	

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#### EXAMPLE 1

A test to demonstrate low temperature operability requires the fatty acids to remain bright and clear after three days storage at 23°F (-5°C).

10 **Table 1** compares the performance of different FAC samples in this test.

Table 2 compares the physical properties of the three samples.

Sample A:

FAC 1

Sample B:

FAC 1 + Solvent

15 Sample C:

FAC 1 + Solvent + Wax Modifier (flow improver)

Rating Scale: 1 = Bright and Clear

2 = Cloudy or < 10% ppt.

3 = 10-20% ppt.

4 = 20-50% ppt.

5 = 50-95% ppt.

6 = solid

# Table 1

Sample	After 1 Day @ -5°C	After 3 Days @ -5°C	After 5 Days @ -5°C	After 7 Days @ -5°C
Α	6	6	6	6
В	4	4	4	4
С	1	1	1	1

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**Table 2 Comparison of Physical Properties** 

	Sample A	Sample B	Sample C
Flash Point °F (°C)	392 (200)	200 (93)	208 (97)
Pour Point °F (°C)	10 (-12)	5 (-15)	-11 (-23)
Cloud Point °F (°C)	42.8 (6)	15.8 (-9)	-5.8 (-21)
Density(Lbs/gal)	7.55	7.55	7.55
Specific Gravity 60/60F (16/16C)	0.907	0.907	0.907
Viscosity cst @ 100°F (40°C)	17	12	12
cst @ 68°F (20°C)	27	25	21
cst @ 23°F (-5°C)	solid	128	59

#### **EXAMPLE 2**

Samples A, B, and C, described above were stored overnight at different temperatures to roughly determine what temperatures resulted in solids precipitating from the solutions. These observations are reported in Table 3.

Table 3 Observations after 24-hour storage at decreasing temperatures.

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Sample	20°C (68°F)	15°C (59°F)	10°C (50°F)	5°C (41°F)	0°C (32°F)
Α	Clear & bright	clear & bright	45 % layer of clear slushy crystals	45 % layer of solids	100% solid
B	Clear & bright	clear & bright	clear & bright	15% layer of crystals	45% layer of crystals
<u>c</u>	Clear & bright	clear & bright	clear & bright	clear & bright	clear & bright

#### **EXAMPLES 3-5**

Samples in accordance with the present invention were studied by differential scanning calorimetery (DSC). The DSC procedure was conducted in a TA Instruments 2010 in a standard DSC crucible. The samples were studied at a heating or cooling rate of 1°C/min. The samples were also studied isothermally at -7°C.

# EXAMPLE 3 - The Effect of Flow Improver on Different FACs

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#### Example 3.1

FAC	Amount of FAC	Flow Improver	Amount of Flow Improver	Phase at -7°C
1	99.0	AZ 253	1.0	Liquid
2	99.0	AZ 253	1.0	Liquid
3	99.0	AZ 253	1.0	Liquid

AZ 253 is a cloud point depressant available from Elf and described in GB-A-2121808.

WO 01/38461

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It can be seen that the flow improver prevented crystallisation of each of the fatty acids tested at low temperature.

## Example 3.2

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Samples of A, B and C were prepared using a number of different fatty acids. The composition of the samples were as follows

Sample A 100 % fatty acid

Sample B 75 % fatty acid + 25% solvent added

10 Sample C 75 % fatty acid + 20% solvent + 5% wax modifier (cold flow improver)

Samples were prepared and placed in a controlled temperature bath. The temperature was lowered daily until it reached 0°C where it was held for two days, then lowered to – 5°C, where it remained constant throughout the remaining test days. Samples were evaluated and rated each day.

Rating: 1 = clear and bright

5 = 25 - 49% crystals

2 = cloudy

6 = 50 - 74% crystals

3 = < 10% crystals

7 = 75 - 100% crystals

4 = 10 - 24% crystals

8 = solid

Sample	Fatty Acid				7	emperatu	re			
		20°C Day 1	10°C Day 2	0°C Day 3	0°C Day 4	-5°C Day 5	-5°C Day 6	-5°C Day 7	-5°C Day 8	-5℃ Day 9
Α	1	1	1	3	3	3	1.	-	1.	-
A B		1	1	3	4	7	1.	1.	1.	1
C		1	1	2	2	2		1.	1.	† <del>.</del>
A	2	1	8	8	8	8	1.	1.		1
8		1	1	7	7	7		<del> </del>	† <del>.</del> –	1
С		1	1	2	2	2	2	2	3	3
Α	3	6	7	7	7	7	-	-	1-	1-
В		1	6	7	7	7	· -	-	-	+
C		3	3	1	1	1	1	1	1	1
Α	4	1	1	1	3	4	<del>                                     </del>	<del>                                     </del>	<del>                                     </del>	<del>                                     </del>
В		1	1	1	1	1	1	1	1	3
С		1	1	1	1	<del>                                     </del>	1	1	1	1
Α	5	1	1	8	8	8	<del>                                     </del>	-	<u> </u>	<del>-</del>
В		1	1	1	1	1	1	1	1	1
С		1	1	1	1	1	1	1	<del>                                     </del>	1
Α	6	1	1	5	7	7	<del>                                     </del>	-	<del>                                     </del>	<del>  -</del> -
В		1	1	1	1	3	-	<del>                                     </del>	<del>                                     </del>	<del></del>
С	7	1	1	1	2	2	2	2	2	2
A	7	1	1	1	3	6				
В	7	1	1	<del>                                     </del>	1	1	1	3	7	7
С	7	1	1	<del>    -                                  </del>	1					
<u> </u>		] ]		11	2	2	2	2	2	2

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# Key to Fatty Acids

- 1 = Sylfat 1F from Arizona Oulu, Finland
- 2 = Sylfat FA2 from Arizona Panama City, Florida
- 3 = Sylfat FA2 from Arizona Panama City, Florida
- 5 4 = Sylfat 1F from Rosilr Services Ltd., Eaglescliffe Stockton-on-Tees
  - 5 = Tall Oil Mixture from Arizona Panama City, Florida FA-7002
  - 6 = Sylfat 2 from Arizona Oulu, Finland
  - 7 = Sylfat 2LT from Arizona Oulu, Finland
- These data demonstrate that the system of the present invention may inhibit the crystallisation of a broad range of fatty acid products. Furthermore the data demonstrate that improvement afforded by dilution with a commonly used solvent is not as effective as that provide by the present invention.

# 15 EXAMPLE 4 - The Effect of Amount of Flow Improver

## Example 4.1

FAC	Amount of FAC	Flow Improver	Amount of Flow Improver	Phase at -7°C
2	100.0	AZ 253	0.0	Solid
2	99.5	AZ 253	0.5	Liquid
2 .	95.0	AZ 253	5.0	Liquid

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It can be seen that the flow improver prevented crystallisation of the fatty acid when compared to the base line in the absence of the flow improver.

FAC	Amount of FAC	Flow Improver	Amount of Flow Improver	Crystallisation Temperature (°C)	ΔΤ
3	100.0	AZ 253	0.0	-1.7	
3	99.9	AZ 253	0.1	-5.1	-3.4
3	99.5	AZ 253	0.5	-6.9	-5.2
3	99.0	AZ 253	1.0	-8.5	-6.8
3	95.0	AZ 253	5.0	-9.6	-7.9

 $\Delta T$  represents the difference between the crystallisation temperature of the composition and the crystallisation temperature of the given fatty acid in the absence of the flow improver.

The results of the DSC are shown in Figure 1.

It can be seen that the flow improver prevented crystallisation of the fatty acid when compared to the base line in the absence of the flow improver. An improvement was noted at a concentration of 0.1 % flow improver. The improvement was increased as the concentration of flow improver increased

Example 4.2

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Samples of A to E were prepared using a number of flow improvers. The composition of the samples were as follows

10 A 85% Fatty Acid; 14.9% solvent; 0.1% flow improver

B 85% Fatty Acid; 14.5% solvent; 0.5% flow improver

C 85% Fatty Acid; 14% solvent; 1% flow improver

D 85% Fatty Acid; 13% solvent; 2% flow improver

E 85% Fatty Acid; 10% solvent; 5% flow improver

Samples were prepared and placed in a controlled temperature bath. The temperature was lowered daily until it reached -5°C, where it remained constant throughout the remaining test days. Samples were looked at and rated each day.

20 Rating: 1 =

1 = clear and bright 5

5 = 25 - 49% crystals

2 = cloudy

6 = 50 - 74% crystals

3 = <10% crystals

7 = 75 - 100% crystals

4 = 10 - 24% crystals

8 = solid

Sample	Flow	Temperature Temperature									
	Improver	20°C Day 1	15°C Day 2	10°C Day 3	5°C Day 4	0°C Day 5	-5℃ Day 6	-5°C Day 7	-5°C Day 8	-5°C Day 9	-5°C Day 10
100% FA	-	1	1	5		1.		1.		1.	
85% FA 15% solvent	•	1	1	1	1	5		1.		1.	
A	1	1	1	1	1	1	1	3	1.	1-	
В	]	1	1	1	1	1	2	2	3	1.	•
С	]	1	1	1	1	. 2	2	2	4	•	·
D		1	1	1	1	2	2	3	-	-	1.
E		1	2	2	2	2	2	2	3	-	
Α	2	1	1	1	1	3	-	-	-	-	-
В	]	1	1	1	1	1	3	-		-	-
С	}	1	1	1	1	1	1	1	1	1	1
D	]	1	2	1	1	1	1	1	1	1	1
Ε .	<u> </u>	1	1	1	1	1	1	1	1	1	1
A	3	1	1	1	11	1	3			-	-
B	]	1	1	1	1	1	1	3	-	•	
С	]	1	1	1	1	1	1	1	1	1	1
D	]	1	1	1	1	1	1	3		•	•
E	<u>L</u>	1	1	1	1	1	11	1	1	1	1

19

Α	4	1	1	1	1	1	3			<b>-</b>	
В	]	1	1	1	1	1	3			-	-
С	]	1	1	1	1	1	1	4	-		
0	]	1	1	1	1	1	1	1	1	4	
E	1	1	1	1	1	1	1	1	1	3	

#### Key to Flow Improvers

Commercial Cloud Point Depressant Terpolymer of ethylene, methacrylate & succinimide

2 Commercial Wax Anti-Settling Additive
Methylene linked alkyl phenols & low molecular weight poly methacrylate

3 Pour Point Depressant Comb Polymer Poly Methacrylate

4 Commercial Cold Flow Improver Ethylene Vinyl Acetate Copolymers

These data demonstrate that a number of different flow improvers at different concentrations may inhibit the crystallisation of fatty acid products. Furthermore the data demonstrate that improvement afforded by dilution with a commonly used solvent is not as effective as that provided by the present invention.

# **EXAMPLE 5 - The Effect of Different Flow Improvers**

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#### Example 5.1

FAC	Amount of FAC	Flow Improver	Amount of Flow Improver	Crystallisation Temperature (°C)	ΔΤ
1	99.5	CPD-5	0.5	-19.4	-5.4
1	99.5	PF 511	0.5	-18.2	-4.2
1	99.5	RL 830	0.5	-18.6	-4.6
1	99.5	V 311	0.5	-19.5	-5.5
1	99.5	AZ 253	0.5	-19.5	-5.5
3	99.5	AZ 253	0.5	-8.0	-6.3
3	99.5	CP 8327	0.5	-7.9	-6.2
3	99.5	V 311	0.5	-8.1	-6.4

CPD-5 is a cloud point depressant available from Starreon, US

15 PF 511 is a cloud point depressant available from Paramins, US

RL 830 is a cloud point depressant available from Elf, France.

V 311 (Dodiflow V 311) is a cloud point depressant available from Clariant, Switzerland. CP 8327 a cloud point depressant is available from Elf, France.

The results of the DSC of FAC 1 are shown in Figure 2. The results of the DSC of CP 8327 and V311 with FAC 3 are shown in Figure 3.

It can be seen that each of the flow improvers tested prevented crystallisation of both of

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the fatty acids at low temperature.

#### Example 5.2

FAC	Amount of FAC	Flow Improver	Amount of Flow Improver	Crystallisation Temperature (°C)	ΔΤ
1	99.5	CFPP	0.5	-18.2	-4.2
1	99.5	ES 3217	0.5	-17.3	-3.3
1	99.5	AZ 253	0.5	-19.5	-5.5
3	95.0	OFI 7250	5.0	-9.8	-8.1
3	95.0	AZ 253	5.0	-9.6	-7.9

CFPP is Dodiflow 4300, a cold filter plugging point additive (CFPP) available from Clariant, Switzerland.

ES 3217 is a wax anti-settling additive available from BASF, Germany.

OFI 7250 is a cold filter plugging point additive available from The Associated Octel, UK.

The results of the DSC of OFI 7250 are shown in Figure 3. The results of the DSC of ES 3217 are shown in Figure 4.

It can be seen that each of the flow improvers tested prevented crystallisation of both of the fatty acids at low temperature.

#### Example 5.3

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Samples of A and B were prepared using a number of flow improvers. The composition of the samples were as follows

A 85% Fatty Acid; 14.9% solvent; 0.1% flow improver

B 85% Fatty Acid; 14.5% solvent; 0.5% flow improver

Samples were prepared and placed in a controlled temperature bath. The temperature was lowered daily until it reached -5°C, where it remained constant throughout the remaining test days. Samples were looked at and rated each day.

Rating: 1 = clear and bright 5 = 25 - 49% crystals

2 = cloudy 6 = 50 - 74% crystals

30 3 = <10% crystals 7 = 75 - 100% crystals

4 = 10 - 24% crystals 8 =solid

Sample	Flow	Temperature									
	Improver	20°C	15℃	10°C	5°C	10°C	-5°C	-5°C	-5°C	I-5°C	I-5°C
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 9	Day 10
100% FA	•	1.									
	<del> </del>	1	1	5		<u> -</u>	<u> </u>	<u> </u>	1-	<u> -</u>	1
85% FA	-	l .		1	Í	·					
15% solvent		11	1	1	1	5	١-	-	<u>  -                                   </u>	<u> -</u>	<u>  •                                     </u>
Α	] 1	1	1	1	1	1	1	3	•		-
В		1 1	1	1	1	1	2	2	3	•	1:
Α	2	1	1	1	1	3	]-	-	1.		
В		1	1	1	1	1	3	•	1-	-	
A	3	1	1	1	1	1	3	-		1.	1-
В		1	1	1	1	1	1	3	1-	1.	
Α	4	1	1	1	1	1	3	-	1.	1.	-
В		1	1	1	1	1	3	1.	-	-	1.
A	5	1	1	1	1	1	6	-	-	1.	
В	1	1	1	1	1	1	3	1-	1-	1.	1.
Α	6	1	1	1	1	1	2	3	-	1.	
В	1	1	1	1	1	2	2	2	2	3	† <del>.          </del>
Α	7	1	1	1	2	1	2	1	1	1	1
В	1	1	1	1	1	1	2	2	4	<del>                                     </del>	<del> </del>
Α	8	1	1	1	1	2	3	-	1.	1.	<del> </del> -
В		1	2	2	2	2	2	2	2	2	2
Α	9	1	1	1	1	1	3	-	1.	1-	-
В		1	1	1	1	1	1	3	-	+-	-
A	10	1	1	1	1	li –	3	-	<del>                                     </del>	-	-
В		1	1	1	1	1	1	1	3	1.	<del>                                     </del>
A	11	1	i	1	5	<del>                                     </del>	-	<del>                                     </del>	-		<del>-</del>
В	┥''	1	11	1	5	<del>-</del> -	-	<del>  -</del>	ļ. —	1	<del>-</del>
Ā	12	1	1	1	5	<del></del>		-			
В	<b>⊣</b> '*	1	1	1	5		-	<del> </del>	ļ -	ļ.	
Ā	13	1	1	1	1	1	4		ļ -	ļ-	ļ <del>-</del>
B		1	1	1	1			-	·	<del> </del>	-
A	14	1	1	1		1	1	1	1	1	1
<del>B</del>	' · <del></del>		<del></del>		1	1	6	-	-	<u> -</u>	-
A	16	1	1	1	1	1	1	1	1	1	1
B	15	1	1	1	1	1	1	3	ļ <u>-</u>		•
D		1	1	1	1	2	2	2	2	2	2

## Key to Flow Improvers

- 1 Commercial Cloud Point Depressant
  Terpolymer of ethylene, methacrylate & succinimide
- 2 Commercial Wax Anti-Settling Additive Methylene linked alkyl phenois & low molecular weight poly methacrylate
- 3 Pour Point Depressant
  - Comb Polymer Poly Methacrylate
- 4 Commercial Cold Flow Improver Ethylene Vinyl Acetate Copolymers
- 5 Commercial Pour Point Depressant
- Comb Polymer Poly Methacrylate
  Commercial Cold Flow Improver
- Ethylene Vinyl Acetate Copolymers
- 7 Commercial Cloud Point Depressant Terpolymer of ethylene, methacrylate & succinimide
- 8 Commercial Cold Flow Improver Alkyl Phenol Copolymer
- 9 Commercial Cold Flow Improver
- Ethylene Vinyl Acetate Copolymers
  Commercial Cold Flow Improver
  - Terpolymer of Ethylene with Ethylene Vinyl Acetate
- 11 Wax Dispersant A Comb Polymer
- 12 Wax Dispersant B Alkylphenol Resin

22

- 13 Wax Dispersant C
  Oxalkylated Amine with an Alkyl Phenol Resin
- 14 Commercial Cloud Point Additive Fumarate Vinyl Acetate
- 15 Commercial Cloud Point Additive Alkyl Phenol Resin

These data demonstrate that a number of different flow improvers having differing chemistries may inhibit the crystallisation of fatty acid products. Furthermore the data demonstrate that improvement afforded by dilution with a commonly used solvent is not as effective as that provided by the present invention.

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

23

#### **CLAIMS**

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1. Use of a flow improver for the prevention and/or inhibition of the crystallisation of a fatty acid from a composition comprising the fatty acid.

2. A composition comprising a fatty acid and a flow improver.

- A use or composition according to claim 1 or 2 wherein the flow improver is present in the composition in an amount of less than 10 wt%, preferably 0.01 to 5.00 wt.%, preferably 0.05 to 3.00 wt.%, preferably 0.10 to 2.00 wt.%, based on the total weight of the composition.
- A use or composition according to claim 1, 2 or 3 wherein the flow improver is selected from wax modifiers, cold flow improvers, pour point depressants, wax
   appearance temperature depressants, cold filter plugging point (CFPP) depressants, low temperature flow test (LTFT) temperature depressants
  - 5. A use or composition according to claim 4 the flow improver is selected from wax modifiers, cold filter plugging point (CFPP) depressants and mixtures thereof.

6. A use or composition according to claim 4 or 5 wherein the wax modifier is selected from cloud point depressants, wax anti-settling additives and mixtures thereof.

- 7. A use or composition according to claim 4, 5 or 6 wherein the flow improver is a diesel fuel cloud point depressant.
  - 8. A use or composition or use according to any one of the preceding claims wherein the flow improver is selected from ethylene-unsaturated ester copolymers, comb polymers, polar nitrogen compounds, hydrocarbon polymers and mixtures thereof.
  - 9. A use or composition according to claim 8 wherein the hydrocarbon polymer is dissolved or is dispersed in an aromatic solvent.
- 10. A use or composition according to claim 8 or 9 wherein the ethylene-unsaturated step ester copolymer is or comprises a copolymer of ethylene with an ethylenically

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unsaturated ester, derivatives and mixture thereof.

- 11. A use or composition according to claim 8, 9 or 10 wherein the comb polymer is or comprises a copolymer of (i) maleic anhydride, fumaric acid, itaconic acid or a mixture thereof and (ii) another ethylenically unsaturated monomer.
  - 12. A use or composition according to any one of claims 8 to 10 wherein the polar nitrogen compound is or comprises an oil-soluble polar nitrogen compound carrying one or more, preferably two or more, substituents.
  - 13. A use or composition according to claim 12 wherein the polar nitrogen compound is capable of acting as a wax crystal growth inhibitor in a fuel.
- 14. A use or composition according to any one of claims 8 to 13 wherein the hydrocarbon polymer is obtained or is obtainable directly from a monoethylenically unsaturated monomers or indirectly by hydrogenating polymerised polyunsaturated monomers, including isoprene and butadiene.
- 15. A use or composition according to any one of the claims 8 to 13 wherein the hydrocarbon polymer is or comprises a terpolymer of (i) linear C16 or C18 alkene, (ii) a C18 methacrylate or acrylate, and (iii) a succinimide having a C18 carbon chain.
  - 16. A use or composition according to claim 15 wherein the components (i), (ii) and (iii) are present in a ratio of approximately 1:1:1.
  - 17. A use or composition according to any one of the preceding claims wherein the fatty acid is obtained or is obtainable from rapeseed oil, coriander oil, soybean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef oil, tallow oil, fish oil, and mixtures thereof.
  - 18. A use or composition according to any one of the preceding claims wherein the fatty acid is selected from saturated, unsaturated, poly-unsaturated fatty acids, and mixtures thereof.
- 35 19. A use or composition according to any one of the preceding claims wherein the

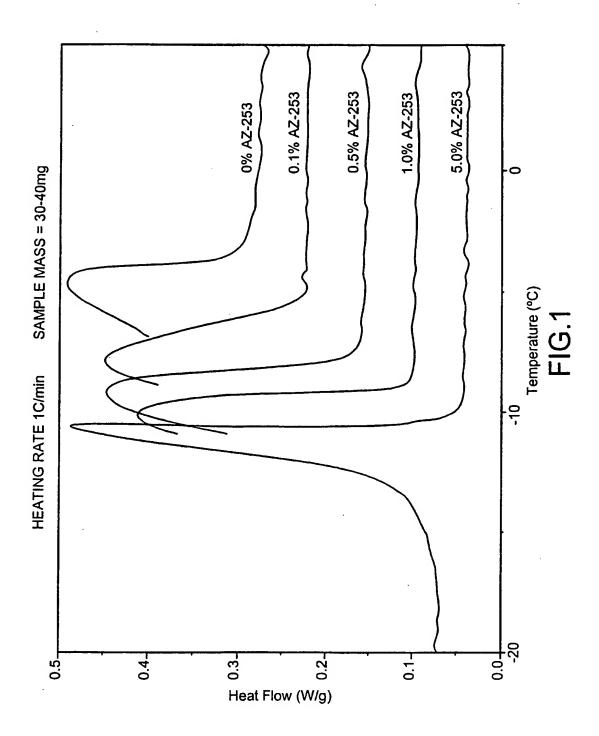
fatty acid is selected from lauric acid, rosin acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid, erucic acid, eicosapentaenoic acid and mixtures thereof.

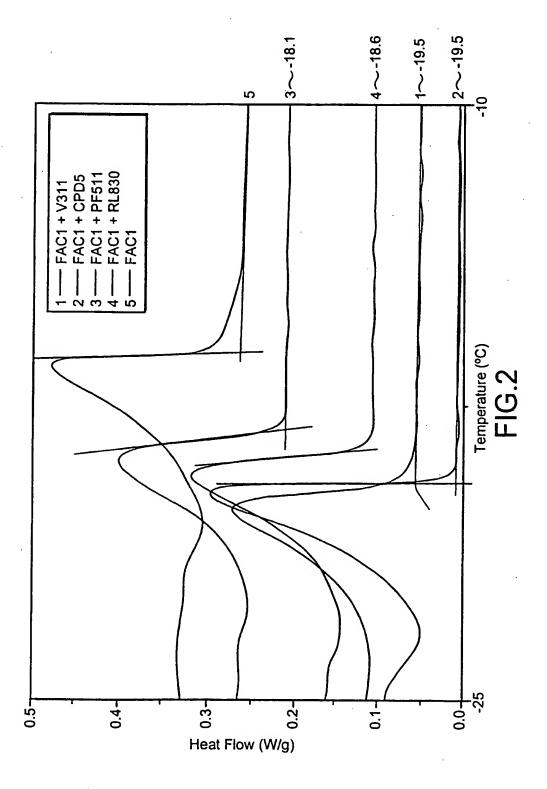
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- 20. A use or composition according to any one of the preceding claims wherein the fatty acid is selected from mixtures of fatty acids having a chain length of from 12 to 22 carbon atoms
- 10 21. A use or composition according to any one of the preceding claims wherein the fatty acid is selected from mixtures of fatty acids having a chain length of from 16 to 18 carbon atoms.
- 22. A use or composition according to any one of the preceding claims wherein the fatty acid is selected from mixtures of fatty acids consisting of 10-80% oleic monounsaturated fatty acid, 10-80% linoleic di-unsaturated fatty acid, 0-80% saturated fatty acid and 0-80% rosin acid.
- 23. A use or composition according to any one of the preceding claims wherein the fatty acid is selected from mixtures of fatty acids consisting of approximately 65% linoleic di-unsaturated fatty acid, approximately 30% oleic mono-unsaturated fatty acid, approximately 2% saturated fatty acids and <2% rosin acid.
  - 24. A use or composition according to claim 22 or 23 wherein the saturated fatty acids are selected from stearic acid (C16) and palmitic (C18) acid.
    - 25. A use or composition according to any one of the preceding claims wherein the fatty acid is a tall oil fatty acid.
- 30 26. A composition according to any one of the preceding claims wherein the composition comprises one or more additional components selected from detergents, one or more additional cold flow improvers antioxidants, corrosion inhibitors, dehazers, demulsifiers, antifoaming agents, cetane improvers, Conductivity improvers, metal deactivators, dyes, chemical markers, cosolvents, package compatibilisers, carrier oils, biocides, surfactants, buffers, lubricity additives including polycarboxylic acids, and

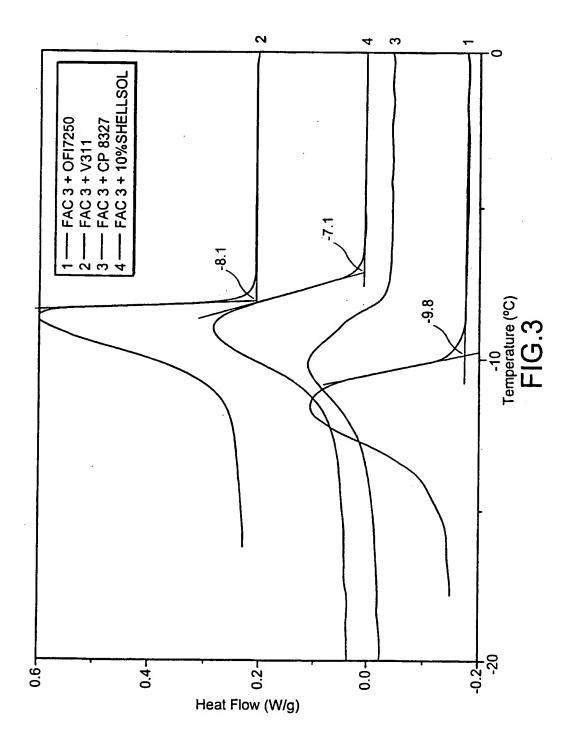
mixtures thereof.

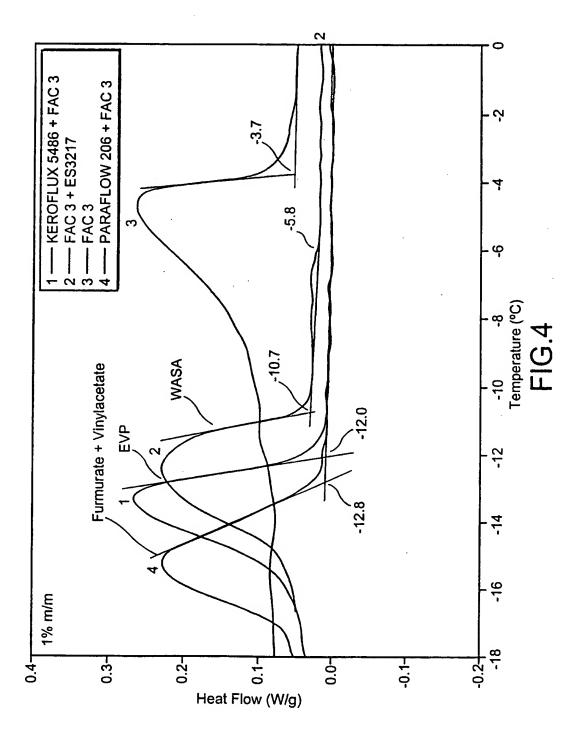
- 27. A composition according to any one of the preceding claims wherein the composition is an intermediate in the production of or is utilised in an adhesive, alkyd resin, detergent, soap, cleaner, fuel additive, ink, coating, lubricant, metalworking fluid, mining fluid, oil field exploration, paper treatment, polyamide resin, road building, rubber processing, corrosion inhibitor, surfactant or fuel.
- 28. A method for preventing and/or inhibiting the crystallisation of a fatty acid from a composition comprising the fatty acid, the method comprising the step of contacting the composition with a flow improver.
  - 29. A method according to claim 29 characterised by any one of claims 3 to 28.
- 15 30. A fuel comprising a composition as defined in any one of claims 2 to 27.
  - 31. A fuel according to claim 30 wherein the fuel is selected from gasolines including motor, aviation, tractor, and marine fuels, middle distillate fuels including fuels, diesel fuels, marine fuels, and heating oils, and biofuels including a rapeseed methyl ester and vegetable oil; and mixtures thereof.
  - 32. A fuel additive consisting of a composition as defined in any one of claims 2 to 27.
- 25 33. A lubricant composition consisting of a composition as defined in any one of claims 2 to 27.
  - 34. A lubricating improver consisting of a composition as defined in any one of claims 2 to 27.

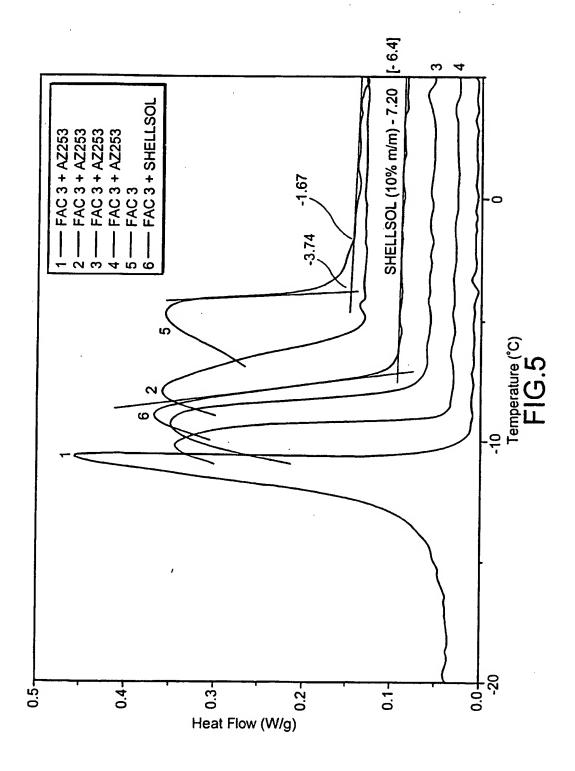




**SUBSTITUTE SHEET (RULE 26)** 









Inte. .ional Application No PCT/GB 00/04328

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C10L1/14 C10M161/00 C10M171/00 C10M169/04 //(C10M161/00,127:06,129:40,129:60,129:62,133:16,143:00,145:02, 149:06),(C10M169/04,105:24,127:06,133:16,143:00,145:02,149:06),

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUM	ENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199827 Derwent Publications Ltd., London, GB; Class H06, AN 1998-306256 XP002160441 & JP 10 110175 A (KAO CORP), 28 April 1998 (1998-04-28) See English translation of the whole patent. abstract	1-10,12, 14, 17-21, 26-34
X	US 5 755 834 A (CHANDLER JOHN E) 26 May 1998 (1998-05-26) the whole document/	2-14,26, 27,30-32

X Further documents are listed in the continuation of box C.	X Patent family members are listed in annex.
Special categories of cited documents:      'A' document defining the general state of the art which is not considered to be of particular relevance      'E' earlier document but published on or after the international filing date      'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)      'O' document reterring to an oral disclosure, use, exhibition or other means      'P' document published prior to the international filing date but later than the priority date claimed	<ul> <li>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</li> <li>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</li> <li>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</li> <li>*&amp;* document member of the same patent family</li> </ul>
Date of the actual completion of the international search  15 February 2001	Date of mailing of the international search report 23/02/2001
Name and malling address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  De La Morinerie, B

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Int. :lonal Application No PCT/GB 00/04328

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A. CLASS IPC 7	IFICATION OF SUBJECT MATTER C10N30:02		
According t	to International Patent Classification (IPC) or to both national class	ification and IPC	
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Documenta	ation searched other than minimum documentation to the extent the	at such documents are included in the field:	s searched
Electronic	data base consulted during the international search (name of data	base and, where practical, search terms us	sed)
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the	relevant passages	Relevant to claim No.
X	EP 0 155 171 A (EXXON RESEARCH CO) 18 September 1985 (1985-09-	ENGINEERING 18)	2-10,12, 13, 17-21, 26,27, 30-32
	the whole document		30-32
X	GB 2 288 815 A (EXXON CHEMICAL I INC) 1 November 1995 (1995-11-0)		2-8,11, 14, 17-21, 26,27, 33,34
	page 15, paragraph 2; claims 1,5 page 18, paragraph 4 -page 19, p	o,6 baragraph 1	
		-/	
	·		
		•	
X Furti	her documents are listed in the continuation of box C.	Patent family members are liste	ed in annex.
° Special ca	stegories of cited documents:	"T" later document published after the in	elernational filing date
consid	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international	or priority date and not in conflict wi cited to understand the principle or invention  X* document of particular relevance; the	th the application but theory underlying the
"L" docume which citation	and the control of th	cannot be considered novel or cann involve an inventive step when the c  "Y" document of particular relevance; the cannot be considered to involve an	of be considered to document is taken alone claimed invention inventive step when the
other r	means ent published prior to the international filing date but nan the priority date claimed	document is combined with one or r ments, such combination being obv in the art.  *&* document member of the same pater	ous to a person skilled
Date of the	actual completion of the international search	Date of mailing of the international s	
1!	5 February 2001		
Name and n	nailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2	Authorized officer	
	NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De La Morinerie,	В

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ional Application No PCT/GB 00/04328

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X GB 2 308 129 A (LUBRIZOL CORP) 18 June 1997 (1997-06-18)	2-8,10, 11, 17-27, 30-34
examples 1,6-9  DE 26 12 757 A (CHEMISCHE FABRIEK SERVO B	2.6.0
V) 29 September 1977 (1977-09-29) the whole document	2-6,9, 17-27
WO 99 36489 A (BAKER HUGHES INC) 22 July 1999 (1999-07-22)	1-6,8,9, 12, 17-21,
claims 1,6	26-34
DE 42 25 951 A (LEUNA WERKE AG) 10 February 1994 (1994-02-10) the whole document	2-8,10, 17-21, 26,27, 30-32
A EP 0 780 460 A (EXXON RESEARCH ENGINEERING CO) 25 June 1997 (1997-06-25) the whole document	22-25
EP. 0 829 527 A (EXXON RESEARCH ENGINEERING CO) 18 March 1998 (1998-03-18) the whole document	22-25
US 4 929 375 A (ROSSIO CHARLES E ET AL) 29 May 1990 (1990-05-29)	
A EP 0 890 631 A (EXXON CHEMICAL PATENTS INC) 13 January 1999 (1999-01-13)	
A EP 0 626 442 A (LUBRIZOL CORP) 30 November 1994 (1994-11-30)	
A EP 0 651 044 A (LUBRIZOL CORP) 3 May 1995 (1995-05-03)	
GB 2 121 807 A (INST FRANCAIS DU PETROL;ELF FRANCE) 4 January 1984 (1984-01-04)	
·	

Information on patent family members

Int. tional Application No PCT/GB 00/04328

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 10110175	A	28-04-1998	NONE	·— .
US 5755834	Α	26-05-1998	NONE	
EP 0155171	A	18-09-1985	US 4569679 A CA 1257477 A DE 3565284 D JP 1846878 C JP 5056398 B JP 61000294 A	11-02-1986 18-07-1989 03-11-1988 07-06-1994 19-08-1993 06-01-1986
GB 2288815	A	01-11-1995	NONE	
GB 2308129	A	18-06-1997	US 5851429 A AU 713217 B CA 2191036 A CN 1158887 A NO 965075 A	22-12-1998 25-11-1999 30-05-1997 10-09-1997 30-05-1997
DE 2612757	Α	29-09-1977	NONE	
WO 9936489	A	22-07-1999	AU 2457799 A EP 1047757 A US 6129772 A	02-08-1999 02-11-2000 10-10-2000
DE 4225951	A	10-02-1994	FR 2694568 A GB 2269824 A,B	11-02-1994 23-02-1994
EP 0780460	Α	25-06-1997	US 5968211 A	19-10-1999
EP 0829527	A	18-03-1998	WO 9811175 A EP 0938533 A NO 991172 A	19-03-1998 01-09-1999 05-05-1999
US 4929375	A	29-05-1990	US 5441654 A US 5510045 A US 5009801 A US 5073280 A US 5223162 A	15-08-1995 23-04-1996 23-04-1991 17-12-1991 29-06-1993
EP 0890631	A	13-01-1999	EP 0885947 A EP 0889111 A EP 0890632 A EP 0892034 A AT 176273 T AU 714453 B AU 4786796 A BR 9607004 A CA 2210991 A DE 69601458 D DE 69601458 T DK 807155 T WO 9623855 A EP 0807155 A ES 2127005 T FI 973196 A JP 10513208 T	23-12-1998 07-01-1999 13-01-1999 20-01-1999 15-02-1999 06-01-2000 21-08-1996 28-10-1997 08-08-1996 11-03-1999 02-09-1999 13-09-1999 08-08-1996 19-11-1997 01-04-1999 01-10-1997 15-12-1998

O Constant

Information on patent family members

Inty ...donal Application No PCT/GB 00/04328

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0890631	A	<del></del>	US	5958089 A	28-09-1999
EP 0626442	A	30-11-1994	AU AU CA DE DE ES	674052 B 5901694 A 2117278 A 69419456 D 69419456 T 2135542 T	05-12-1996 01-12-1994 25-11-1994 19-08-1999 05-01-2000 01-11-1999
EP 0651044	A	03-05-1995	US AU AU CA JP	5338471 A 673104 B 7446694 A 2117957 A 7157790 A	16-08-1994 24-10-1996 04-05-1995 16-04-1995 20-06-1995
GB 2121807	Α	04-01-1984	FR CA DE IT NL US	2528067 A 1200341 A 3320573 A 1164264 B 8301936 A, 4503182 A	09-12-1983 04-02-1986 08-12-1983 08-04-1987 B, 02-01-1984 05-03-1985